

# Trends in Reactive Nitrogen Emissions in Light-duty United States Vehicle Fleets

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## Overview

- $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ),  $\text{NH}_3$  are PM precursors;  $\text{NO}_2$  is an immediate ozone forming pollutant.
- Measured:  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{HC}$ ,  $\text{NO}$ ,  **$\text{NO}_2$**  and  **$\text{NH}_3$** , speed, acceleration, license plate
- Over 67,000 vehicle measurements in 2013 and over 40,000 previous measurements from 2005 and 2008.
- Previous measurement references:  
Burgard et al., *Environ. Sci. Technol.* **2006**, 40, 7018-7022.  
Bishop et al. *Environ. Sci. Technol.* **2010**, 44, 3616-3620.

## Field Sampling Locations



## On-Road Measurement Summary

Location	Dates Sampled	Attempts	Matched	Mean Model Year
Denver	6/1 – 3 2005	5,101	3,695 (72%)	1998.7
Denver	12/12,13 2013 1/4 2014	25,881	19,242 (74%)	2005.2
Tulsa	9/19 - 23 2005	26,627	18,890 (71%)	1999.3
Tulsa	9/30 - 10/4 2013	29,268	21,115 (72%)	2006.3
West LA	3/17 - 21 2008	23,579	17,953 (76%)	2001.2
West LA	4/27 - 5/4 2013	33,807	27,247 (81%)	2004.7

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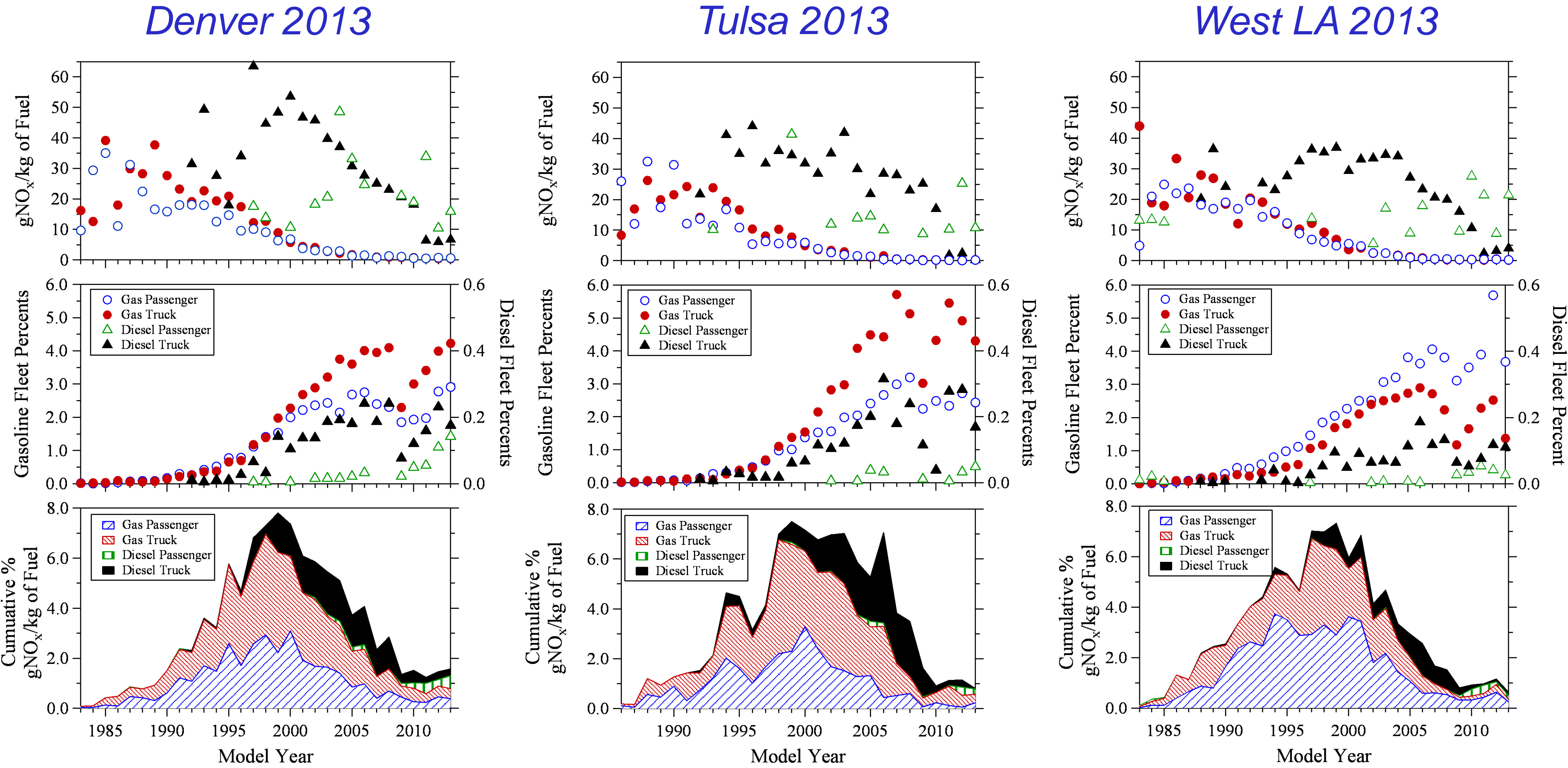
Coordinating Research Council (E-106)



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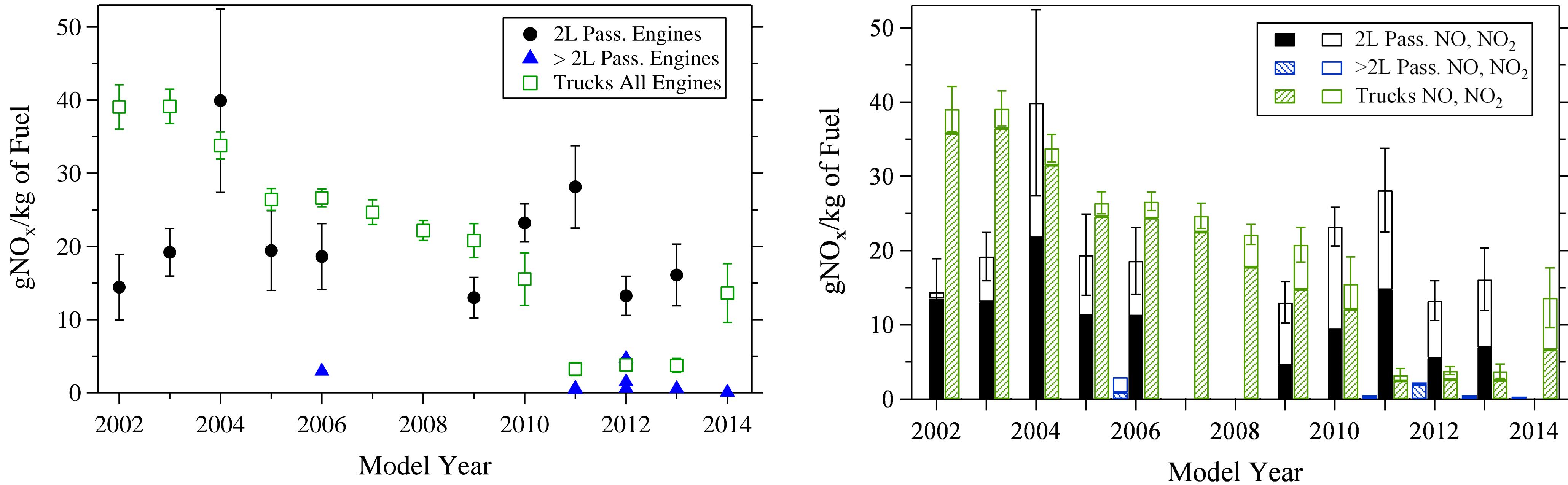
## Measured g/kg of fuel Emissions

Location	Mean g/kg of Fuel Emissions and Standard Errors of the Mean $\text{CO} / \text{HC} / \text{NO} / \text{NO}_2 / \text{NO}_x / \text{NH}_3$ (All Records) $\text{CO} / \text{HC} / \text{NO} / \text{NO}_2 / \text{NO}_x / \text{NH}_3$ (Non-Diesel)	%Reductions $\text{CO} / \text{HC} / \text{NO} / \text{NO}_x / \text{NH}_3$	Mean Speed Mean Acceleration
Denver (2005)	$44.3 \pm 3.0 / 4.0 \pm 0.5 / 3.7 \pm 0.9 / \text{N.A.} / 5.6 \pm 1.3 / 0.45 \pm 0.1$ $44.9 \pm 3.3 / 4.0 \pm 0.5 / 3.2 \pm 0.9 / \text{N.A.} / 5.0 \pm 1.4 / 0.47 \pm 0.1$		25.1 mph 0.7 mph/sec
Denver (2013)	$12.6 \pm 0.9 / 1.8 \pm 0.1 / 2.7 \pm 0.1 / 0.24 \pm 0.02 / 4.4 \pm 0.2 / 0.44 \pm 0.02$ $12.7 \pm 0.9 / 1.8 \pm 0.1 / 2.3 \pm 0.1 / 0.11 \pm 0.02 / 3.6 \pm 0.2 / 0.45 \pm 0.02$	72% / 55% / 27% / 21% / 2% 72% / 55% / 28% / 28% / 4%	22.9 mph 0.01 mph/sec
Tulsa (2005)	$33.5 \pm 0.9 / 2.2 \pm 0.2 / 2.9 \pm 0.2 / \text{N.A.} / 4.4 \pm 0.3 / 0.50 \pm 0.01$ $34.0 \pm 0.9 / 2.2 \pm 0.2 / 2.5 \pm 0.2 / \text{N.A.} / 3.9 \pm 0.2 / 0.51 \pm 0.01$		24.5 mph -0.4 mph/sec
Tulsa (2013)	$13.4 \pm 0.4 / 2.1 \pm 0.3 / 1.5 \pm 0.04 / 0.14 \pm 0.02 / 2.5 \pm 0.1 / 0.43 \pm 0.01$ $13.6 \pm 0.4 / 2.1 \pm 0.3 / 1.3 \pm 0.03 / 0.06 \pm 0.02 / 2.0 \pm 0.1 / 0.44 \pm 0.01$	60% / 5% / 48% / 43% / 14% 60% / 5% / 48% / 49% / 14%	24.3 mph -0.01 mph/sec
West LA (2008)	$21.4 \pm 0.5 / 1.8 \pm 0.1 / 3.8 \pm 0.3 / 0.08 \pm 0.02 / 5.9 \pm 0.4 / 0.79 \pm 0.02$ $21.7 \pm 0.5 / 1.8 \pm 0.1 / 3.5 \pm 0.3 / 0.05 \pm 0.02 / 5.4 \pm 0.4 / 0.80 \pm 0.02$		17.6 mph 1.9 mph/sec
West LA (2013)	$16.4 \pm 0.6 / 2.2 \pm 0.2 / 2.2 \pm 0.1 / 0.16 \pm 0.02 / 3.5 \pm 0.1 / 0.58 \pm 0.02$ $16.6 \pm 0.7 / 2.2 \pm 0.2 / 1.9 \pm 0.1 / 0.11 \pm 0.02 / 3.1 \pm 0.1 / 0.59 \pm 0.02$	23% / -22% / 42% / 41% / 27% 24% / -22% / 43% / 43% / 27%	21.9 mph -0.2 mph/sec



2013 Denver, Tulsa and West Los Angeles  $\text{gNO}_x/\text{kg}$  of fuel emissions by vehicle and fuel type. Gas includes all non-diesels such as hybrids and natural gas vehicles. Trucks have been restricted to weight classes of 1 to 6.

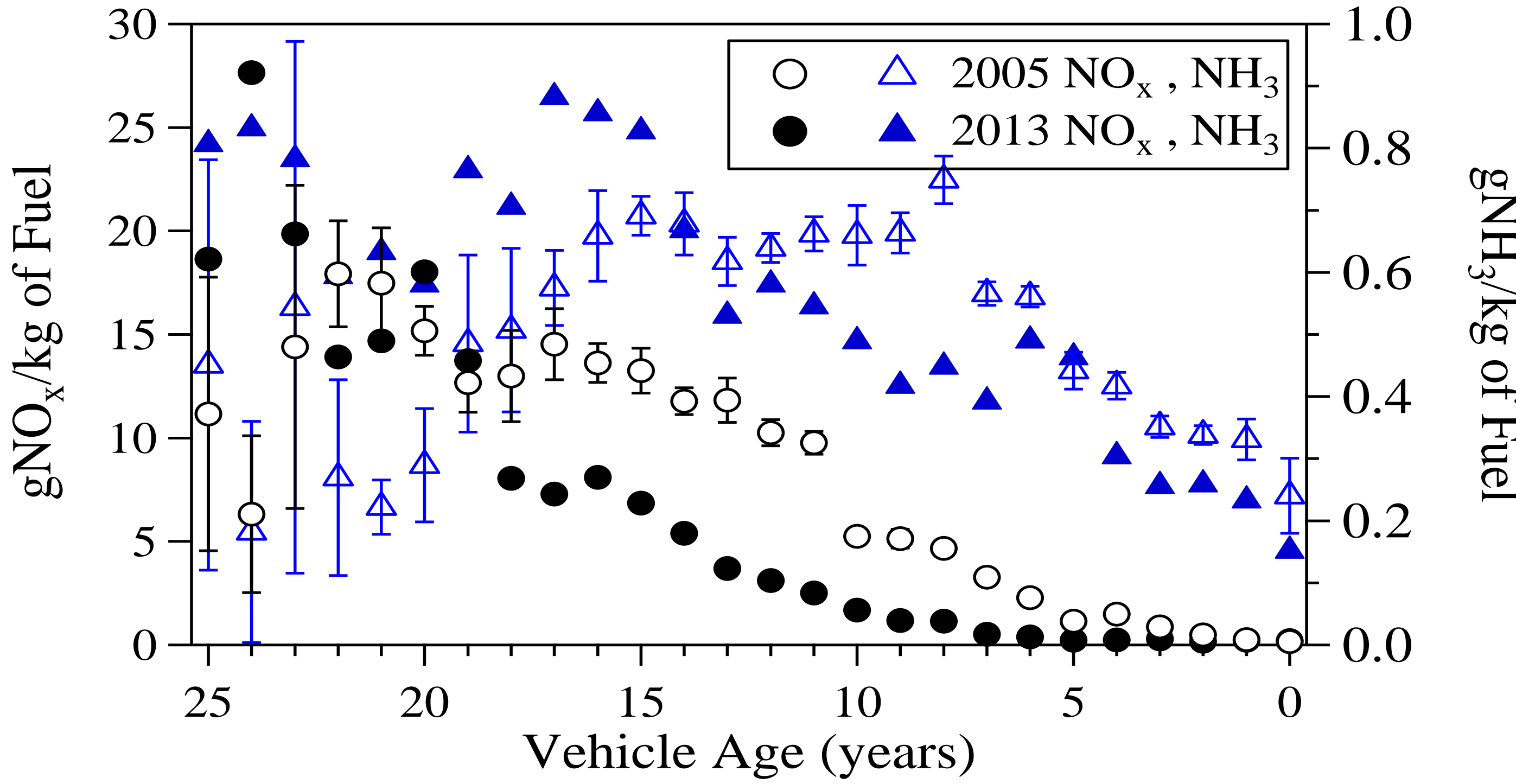
## Three City Combined Diesel Vehicle Measurements



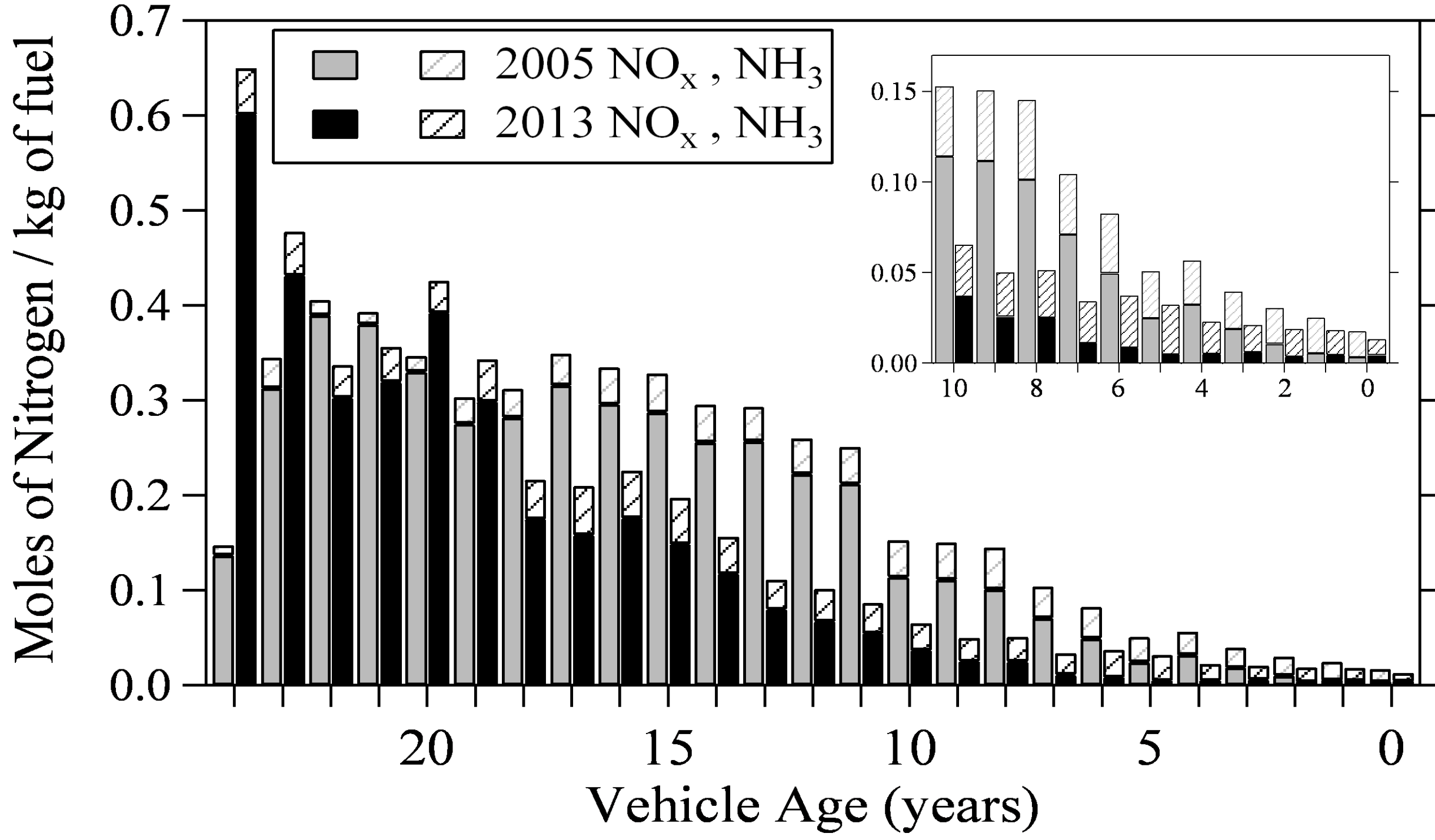
Average  $\text{gNO}_x/\text{kg}$  of fuel for 2L and smaller diesel engine passenger vehicles (circles), diesel trucks (squares) and individual measurements for the diesel passenger vehicles with engines larger than 2L. The uncertainties plotted are standard errors of the mean.

Total  $\text{gNO}_x/\text{kg}$  of fuel subdivided between NO (solid or hatched, converted to NO<sub>2</sub> equivalents) and NO<sub>2</sub> (clear) for 2L and smaller diesel engine passenger vehicles (black), diesel trucks (green) and diesel passenger vehicles with engines > 2L (blue). The uncertainties are standard errors of the mean.

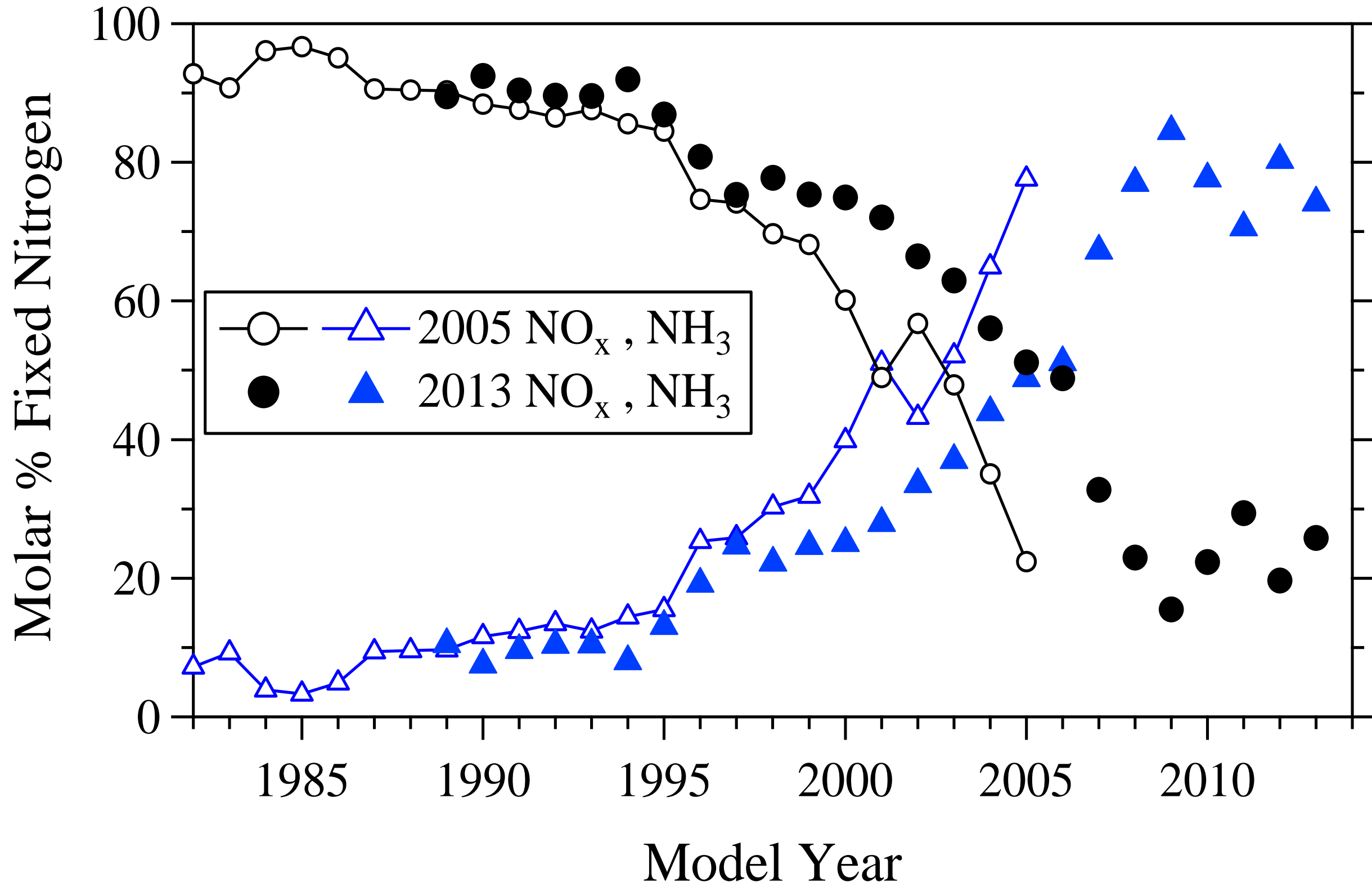
## Tulsa 2005 and 2013 Non-Diesel Reactive Nitrogen Emissions Comparison



Tulsa 2005 (open symbols) and 2013 (filled symbols)  $\text{gNO}_x/\text{kg}$  of fuel (circles, left axis) and  $\text{gNH}_3/\text{kg}$  of fuel (triangles, right axis) emissions versus vehicle age for non-diesel vehicles. Zero year vehicles represent 2006 and 2014 model years respectively. The errors plotted are standard errors of the mean.



Tulsa 2005 and 2013 moles of nitrogen per kilogram of fuel versus vehicle age for non-diesel vehicles. The solid bars represent the moles of nitrogen contributed by  $\text{NO}_x$  and the hatched bars the moles of nitrogen contributed by  $\text{NH}_3$ . The inset graph is an expanded view of the first 10 years.



Molar percent fixed nitrogen for the  $\text{NO}_x$  (circles) and the  $\text{NH}_3$  (triangles) contributions versus model year for the 2005 (open symbols) and 2013 (filled symbols) non-diesel Tulsa data sets.

## Conclusions

- $\text{NO}_x$  emission reductions have outpaced  $\text{NH}_3$  reductions at three long-term measurement sites in the US.
- Non-diesel  $\text{NO}_x$  reductions largely occurred prior to the implementation of the Tier II standards.
- 2009 and newer 2L diesel passenger vehicles showed no  $\text{NO}_x$  emissions reductions with the introduction of the Tier II/LEVII emissions standards due large increases in  $\text{NO}_2$  emissions. For the newest model year vehicles they are a significant  $\text{NO}_x$  source despite their tiny numbers.
- $\text{NH}_3$  reductions have lagged due to modest emissions reductions among the newest model year vehicles and increased emissions from the growing number of older vehicles with active catalytic converters.
- The newest model year vehicles small reactive nitrogen emissions are now predominately  $\text{NH}_3$ .